

T R A N S L A T I O N

(19) JAPANESE PATENT OFFICE (JP)

(12) Official Gazette for Unexamined Patent (A)

(11) Japanese Patent Application Publication: Kokai H11-189925

(43) Publication Date: July 13, 1999

(51) Int. Patent Cl. ⁶	ID. No.	F1	
D 01 F 8/14		D 01 F 8/14	Z
8/06		8/06	

Request for Examination: Not Yet Requested

No. of Claims: 4

OL

Total of Pages: 6

(21) Application Number: H9-353331

(22) Application Date: December 22, 1997

(71) Applicant: 000003159
Toray KK (Toray Co., Ltd.)
No.1 2-ban 2-chome, Nihonbashimuro-machi,
Chuo-ku, Tokyo

(72) Inventors: K. Sugano
c/o Mishima Works, Toray KK,
4845, Mishima City, Shizuoka-ken

A. Taniguchi
c/o Mishima Works, Toray KK,
4845, Mishima City, Shizuoka-ken

(54) [Title of Invention]: **PROCESS FOR THE MANUFACTURE OF SHEATH-CORE
CONJUGATED FIBER**

(57) [Abstract]

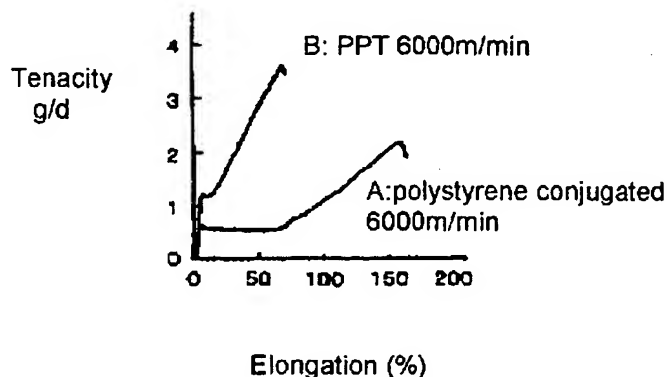
[Problem]

To provide a process for the manufacture of a sheath-core conjugated fiber which comprises using a specific polymer as a core component in the manufacture of poly propylene terephthalate fiber, so as to increase the throughput per unit time, that is, to improve the productivity, and to overcome the undesirable decrease of fiber properties in conventional processes, such as in Young's modulus, elongative elastic recovery and the like.

[Means Used to Solve the Problem]

A process for the manufacture of a sheath-core conjugated fiber which comprises carrying out a sheath-core conjugate spinning using

substantially poly propylene terephthalate as a sheath component polymer and a polymer A as a core component polymer, wherein the polymer A has an elongative viscosity, the temperature dependency of which is greater than that of said poly propylene terephthalate polymer, and said polymer A is present in 0.1-10% by weight of the entire conjugated fiber.



[Claims]

[Claim 1]

A process for the manufacture of a sheath-core conjugated fiber which comprises

carrying out a sheath-core conjugate spinning using substantially poly propylene terephthalate as a sheath component polymer and a polymer A as a core component polymer, wherein

the polymer A has an elongative viscosity the temperature dependency of which is greater than that of said poly propylene terephthalate polymer and said polymer A is present in 0.1-10% by weight of the entire conjugated fiber.

[Claim 2]

A process for the manufacture of a sheath-core conjugated fiber as set forth in Claim 1, wherein the conjugation ratio of the core to sheath components is in the range 5/95-20/80.

[Claim 3]

A process for the manufacture of a sheath-core conjugated fiber as set forth in Claim 1 or Claim 2, wherein the polymer a having an elongative viscosity, the temperature dependency of which is greater than that of poly propylene terephthalate, is a polystyrene-based polymer.

[Claim 4]

A process for the manufacture of a sheath-core conjugated fiber as set forth in any one of the Claims 1-3, wherein the spinning speed is 4000-12000m/min.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a process for the manufacture of a sheath-core conjugated fiber which can contribute to improved productivity and which overcomes the undesirable decrease in fiber physical properties such as in Young's modulus, elongative elastic recovery, and the like.

[0002]

[Prior Art]

Because of their excellent properties, including mechanical properties, polyester fibers are extensively used both in garment applications and in industrial material applications.

[0003]

The conventional process for producing polyester fibers has generally called for melt-spinning the polymer and then stretching, that is, a 2-step process. Such an as-melt-spun fiber has its fiber internal structure undeveloped yet, exhibiting inferior dynamic properties and dimensional stability, and thus requires drawing in a separate step for structure development and set. The draw ratio depends on the melt-spinning conditions, in particular, the take-up rate, so that an excessively high draw ratio setting leads to yarn breakage or a loss of hand, whereby the extent of draw ratio is effectively limited.

[0004]

In general, productivity in a spinning step significantly depends on a per-unit-hour throughput. Because of the foresaid draw ratio limitation in the production of fibers of the desired denier, the denier of the undrawn fiber, or, the spinning throughput is self-limited, an obstacle to improved productivity in the 2-step process.

[0005]

However, in the recent years, a high speed spinning process is being implemented in the industry, calling for take-up rates for polyethylene terephthalate (hereafter PET) of 5000m/min. or higher, and for no drawing, thereby manufacturing practically usable fibers in a single step. The productivity in such a spinning step substantially depends on the per-unit-hour throughput: the higher the speed, the better the productivity in the 1-step process.

[0006]

However, even though such a high speed spinning process, for example, for PET fibers, provides preferred mechanical properties in practice at a spinning speed of about 6000-7000m/min, as the speed is further increased, the fiber tensile properties begin to drop, causing a problem in practice. Therefore, there is a limit in fully taking advantage of the effect of improved productivity.

[0007]

Thus, the throughput has previously been limited, both in the 2-step and in the high speed processes (1-step process). Therefore, if at the same spinning speed, it were possible to suppress the molecular orientation thereby generating a fiber with a greater residual elongation, it would be further possible to increase the spinning rate, that is, to increase the throughput, i.e., for increased productivity.

[0008]

This aspect has been addressed by a spinning process which involves blending the matrix polymer with a small amount of an incompatible polymer. For example, Japanese Patent Application Publication Kokai S58-98414 and Kokai S60-209015 disclose that the addition of 0.15-10% by weight of an incompatible polymer to the matrix polymer leads to a molecular-orientation-suppressed spinning process. Kokai 57-11211 discloses a process of adding a liquid crystalline polymer. Kokai 56-91013, Kokai 57-47912, Kokai 62-21817 also disclose that addition of a small amount of polyolefin polymer to polyester can inhibit molecular orientation.

[0009]

However, these processes, which may suppress the molecular orientation, suffer from a bad effect as a result of the added polymer. For example, if a low softening point polymer such as polystyrene is added, the low melting point polymer present on the surface layer

sometimes causes melt fusion when subjected to a treatment such as a false-twisting process that requires a high temperature heat treatment. Incompatibility sometimes generates cloudiness or adversely affects the color formation of a dyed product. Since it was very difficult to uniformly blend in a small amount of a polymer which is a different type from the polyester, this has tended to cause problems such as blend irregularities, frequent occurrence of yarn breakage, dyeing-irregularities, and the like.

[0010]

On the other hand, poly propylene terephthalate fibers have been well known in Kokai 52-5320, 52-8124, and the like, to exhibit excellent elongative elastic recovery, low Young's modulus, good dyeability, and chemical stability, thereby making the fibers suitable for garment applications.

[0011]

However, the relatively expensive raw material 1,3-propane diol has up to now precluded its use in synthetic fibers.

[0012]

[Problem to be Solved by the Invention]

It is an object of the present invention to provide a process for the manufacture of a sheath-core conjugated fiber which permits enhancing the productivity with increased throughput per unit time for poly propylene terephthalate fibers as well as overcoming the undesirable decrease of fiber properties such as in Young's modulus, elongative elastic recovery, and the like.

[0013]

[Means Used to Solve the Problem]

The process for the manufacture of sheath-core conjugated fibers of this invention so as to attain the above objective comprises carrying out a sheath-core conjugate spinning using substantially poly propylene terephthalate as a sheath component polymer and a polymer A as a core component polymer, wherein the polymer A has an elongative viscosity the temperature dependency of which is greater than that of said poly propylene terephthalate polymer and said polymer A is present in 0.1-10% by weight of the entire conjugated fiber.

[0014]

[Embodiment of the Invention]

The present invention is now explained in detail. A sheath-core conjugated fiber spinning is carried out using substantially poly propylene terephthalate as a sheath component polymer and a polymer A as a core component polymer, wherein the polymer A has an elongative viscosity the temperature dependency of which is greater than that of said poly propylene terephthalate polymer and is present in 0.1-10% by weight of the entire conjugated fiber.

[0015]

The poly propylene terephthalate which is used in this invention is a polyester mainly comprising terephthalic acid as a main acid component and 1,3-propane diol as a main glycol component. It may also contain not more than 20 mole %, more preferably, not more than 10 mole % of other ester-bond forming copolymer components.

[0016]

Copolymerizable compounds include dicarboxylic acids such as isophthalic acid, succinic acid, cyclohexane dicarboxylic acid, adipic acid, dimer acid, sebacic acid, and the like; glycol components such as ethylene glycol, diethylene glycol, butane diol, neopentyl glycol, cyclohexane dimethanol, polyethylene glycol, polypropylene glycol, and the like, without being limited to these listed here.

[0017]

The polymer may also contain a titanium dioxide delusterant, a silica or alumina fine particulate slip agent, a hindered phenol derivative antioxidant, color pigments, and the like.

[0018]

The core component polymer needs to contain a polymer A (hereafter sometimes, simply referred to as polymer A) having an elongative viscosity temperature-dependency greater than that of the sheath component poly propylene terephthalate. The term elongative viscosity temperature dependency is determined as in the following. The sheath component poly propylene terephthalate (hereafter sometimes referred to as simply PPT) and the polymer A to be studied are separately melt spun; and along the spinning yarn line, the yarn temperature ($T(K)$), yarn speed ($V(m/sec)$), and birefringence (Δn) are measured. The following equation is used to calculate the rate of deformation (dV/dx) from the

yarn speed; and spun yarn stress (σ) using the stress optical coefficient from birefringence, thereby calculating elongative viscosity (η) from the deformation rate gradient and the spinning yarn stress. Here, x is the distance (m) from the spinneret.

[0019]

$$\eta = \sigma / (dV/dx)$$

Since the yarn temperature $T(x)$ is also measured, the elongative viscosity temperature dependency can be obtained from the $[1/T(x)] - \log \eta(x)$ diagram.

[0020]

Polymer A, in consideration of its temperature dependency relative to PPT, is particularly preferred to be polystyrene in terms of ease of availability, spinning properties, and so on.

[0021]

The core component may be only a polymer A with an elongative viscosity temperature dependency greater than that of the sheath component PPT or a blend thereof. However, for a polymer application requiring stretchability as in athletic applications, the preferred blend with PPT has polymer A having an elongative viscosity temperature dependency greater than that of the sheath component PPT within such a range in the blending ratio so as not to adversely affect the fiber's physical properties, particularly its elongative elastic recovery. In this case, the ratio of polymer A having a greater elongative viscosity temperature dependency with respect to the core component polymer is substantially greater than with the conventional method where the whole polymer is blended in; this facilitates blending, resulting in a considerable reduction in defects caused by blend irregularities relative to the conventional process.

[0022]

There is no particular limitation as to the core-sheath configuration, which may be a concentric circular core-sheath or an eccentric core-sheath; the core may be more than one or may take a sea-island structure; but the conjugation ratio should preferably be at the core-sheath ratio 5/95-20/80. The particularly preferred range is 7/93-15/85. That is, it is important that the polymer A in the core component be present continuously in a given fixed amount in the

direction of the fiber axis, moreover, it should not be exposed at the fiber surface.

[0023]

The content of polymer A having a greater elongative viscosity temperature dependency should be not more than 10% by weight, preferably not more than 7%, more particularly not more than 5% by weight of the entire conjugated fiber in order for the resultant fiber to essentially exhibit the characteristics, particularly the elongation recovery of PPT fibers.

[0024]

Incidentally, Japanese Patent Application Publication S43-23879 discloses a core-sheath conjugated fiber comprising a thermoplastic amorphous polymer in the core (PMMA) in examples and a thermoplastic crystalline polymer (nylon 6 in an example) in the sheath component. However, this patent merely teaches a core/sheath=amorphous polymer/crystalline polymer, nothing about combinations of polymers having different elongative viscosity temperature dependencies; and the patent is meaningful for cold drawing a fiber wound at a low speed, partially cleaving the core polymer. It thereby teaches nothing about the effect of suppressing molecular orientation caused by high speed spinning or about the development of this effect at a very low level. Furthermore, that patent calls for the conjugation ratio of the core polymer to be at least 20% by weight of the entire conjugated fiber, which will fail to make use of the characteristics of the sheath polymer in that the properties of the core polymer will strongly dominate.

[0025]

In consideration of the processability and process stability in the drawing or draw-false twisting in a 2-step process, it is preferred for the resultant fiber to have been oriented to a certain degree. Therefore, the spinning rate should preferably be 4000m/m or greater. It is further preferred for the rate to be 5000m/min or greater. In order to obtain fibers having tensile properties equivalent to those of the high speed spun fiber obtained by spinning alone, it is normally preferred for the spinning speed to be 7000m/min or greater, more particularly 10000m/min or greater. However, if the spinning rate exceeds 12000m/min, the residual elongation will drop, thereby reducing the success rate for an automatic bobbin switching during windup.

[0026]

Use of the above manufacturing process provides the PPT fiber with a suppressed molecular orientation, based on the mechanism that the spinning stress loading ratio varies between the two polymers on the spinning line (cooling stage). If the polymer A has a higher elongative viscosity temperature dependency than does PPT, the PPT's spinning stress load [distribution] ratio will drop as cooling takes place (or downstream of the spinning line), thereby suppressing the orientation of PPT. For example, the spinning stress loading ratio in a high temperature region beneath the spinneret is polymer A/PPT=30/70, which shifts to polymer A/PPT=70/30 over a relatively low temperature region where 95% attenuation has completed.

[0027]

The extent of orientation suppression can be evaluated, for example, by a wound yarn's birefringence or its residual elongation. However, a sheath-core conjugate yarn requires more time if the birefringence of the sheath section alone is to be measured, so that it is simpler to use the residual elongation as a standard of evaluation.

[0028]

The poly propylene terephthalate fiber obtained by this invention, as with the conventional poly propylene terephthalate fiber, exhibits a low Young's modulus and good elongation elastic recovery so that it can be suitably used as a raw yarn, twisted yarn, or false-twisted yarn for stretch material as in pantyhose, tights, swimming suits, socks, as well as in conventional applications such as inner wear, sportswear, brushes, canvases, and garment applications as in backings, slacks, blouson(Fr.), blouse, and the like, as well as in [industrial] material applications such as in ribbons, tapes, belts, and the like.

[0029]

[Examples]

The present invention is now specifically explained using examples of this invention. The procedures for measurements in these Examples were the following.

[0030]

A. Inherent Viscosity $[\eta]$

Measured at 25°C in orthochlorophenol.

[0031]

B. Stress-Strain Curve (A stress-strain curve was obtained using a tensile machine made by Orientech Company under conditions of a sample length of 200mm and the rate of separation of 200mm/min. The stress value was divided by the initial denier and reported as a tensile stress; and the elongation was divided by the initial sample length to obtain a percent elongation.

[0032]

C. Boiling Water Shrinkage

On a measuring instrument with a frame circumference of 0.5m was wound a sample under an initial load at a rate of 60 rounds/min. to generate a small reel with 10 windings, followed by applying a load 20 times the initial load and the reel length was measured. The load was removed and the sample was immersed for 15 minutes in boiling water at 100°C, followed by air drying and measuring the reel length with a load applied again; the following equation was used to calculate the hot water shrinkage:

[0033]

Hot Water Shrinkage % = $(L_0 - L_1) / L \times 100$

where L_0 : length before dipping (mm)

L_1 : length after [dipping in water] and air drying (mm)

D. Periodic Irregularities in the Fiber Lengthwise Direction

A continuous heat shrinkage irregularity measurement system, FTA-500, manufactured by Toray Engineering Co., Ltd. Was used to measure a continuous wet-heat stress at a measurement temperature of 100°C. The yarn speed was 10m/min. and the chart speed was 6 cm/min.

[0034]

E. Elastic Recovery

A sample was mounted on a constant speed elongation type tensile tester equipped with a recorder with a 20cm grip length under an initial load of 1/30g per denier, and extended at a rate of extension of 10% of the grip length until reaching a designated elongation. Then the load was immediately removed at the same rate and a stress-strain curve was recorded, from which the elongation upon reaching the designated elongation was recorded as α and the recovered elongation at which the

stress dropped to a level equal to the initial load was recorded as β ; the recovery was calculated from the following equation.

[0035]

$$\text{Elastic Recovery \%} = (\beta/\alpha) \times 100$$

Example 1

19.4kg of dimethyl terephthalate and 15.2kg of 1,3-propane diol were ester exchanged in the presence of a tetrabutyl titanate catalyst at 140°C-230°C while distilling off methanol, followed by polymerization for 3 hours under constant temperature conditions at 250°C to generate poly propylene terephthalate having an inherent viscosity $[\eta]$ of 0.89.

[0036]

The poly propylene terephthalate having an inherent viscosity of 0.89 prepared in the above method and a chip-blended mixture of polystyrene (Styron 685, product of Asahi Kasei KK) with this poly propylene terephthalate having an inherent viscosity of 0.89 at a rate of 30/70 (weight ratio) were separately melted, filtered through a stainless steel non-woven fabric filter having an absolute filter diameter of 10 μ , and these melts were spun as a sheath-core conjugate through a concentric circular die, with the polystyrene-blended polymer as the core and the poly propylene terephthalate as the sheath, and extruded using spinneret 1 having 24 orifices. The core-sheath conjugation ratio was 15/85; the ratio of polystyrene to the entire conjugated fiber was 4.5% by weight. The process was controlled in such a way to keep the spinning temperature at 260°C and throughput such that monofilament denier was 2d. The extruded filaments were, as shown in Figure 3, cooled after the extrusion by blowing room temperature air at a rate of 25m/min. from a 1.0m long chimney 2, oiled with an oiling guide 3, which was installed 2m beneath the spinneret, and bundled [collected]. The fiber was entangled by an entanglement-imparting device 4, mounted 2m further downstream, followed by taking up by a first take-up roll 5, mounted 4m below the spinneret at a speed given in Table 1. The fiber was led over a second take up roller 6 and wound up with the rotation speed of the winding machine 8 controlled so that the windup tension measured by a tensiometer 7 remained constant. The speed for the first take up roller 5 was the same as that of the second take up roller 6, which was expressed as a spinning speed as given in Table 1(Runs Nos. 1-5).

[0037]

Stress-strain curves for fibers obtained at spinning rates 6000m/min and 10000m/min are shown in Figure 1 as a curve A and the curve A' in Figure 2, respectively. Table 1 also lists tenacity, elongation, boiling water shrinkage, and periodic [shrinkage] irregularities in the fiber lengthwise direction. Table 1 also shows the Young's modulus and 10% elastic recovery after the fiber was drawn using a conventional hot roll drawing machine under conditions of a draw temperature of 60°C and a set temperature of 130°C so as to reach a 40% elongation.

[0038]

Table 1 shows that the sheath-core conjugation of polystyrene-PPT blend polymer with PPT provides the effect of improved residual elongation throughout the entire region of the spinning speed, without adversely affecting the Young's modulus and elongation elastic recovery after the fibers were drawn. As is clearly shown in the stress-strain curve (Figure 1A), the fiber remained as an undrawn yarn even at the spinning speed 6000m/min. Figure 2A' shows that even at the spinning speed of 10000m/min, unlike the case of 100% PPT, good stress-strain characteristics are obtained. Crystallization also had progressed in the latter spinning speed region to give a fiber which permits a practical application as is without the need for drawing or heat treatment.

[0039]

The Examples were repeated for comparative examples, except for using a single PPT component to carry out a similar spinning to give a wound yarn. Table 2 shows the tenacity, elongation, boiling water shrinkage, and periodic irregularities in the fiber lengthwise direction. As in the case of polyethylene terephthalate, the fiber at a spinning speed of 6000m/min or higher, gives physical properties close to those of drawn yarn.

[0040]

[Table 1]

		Wound Yarn	Drawn Yarn
--	--	------------	------------

		Core Polymer	Conju- gation Ratio % By Weight	Spinning Speed m/min	Tenacity g/d	Elonga- tion %	Boiling Water Shrin- kage %	Periodic Irregul- arities Length- wise Direction (cv%)	Drawn Yarn Young's Modulus (g/d)	10% Elongation Elastic Recovery (%)
EX.	1	Poly- styrene /PPT= 30/70	15	4000	1.8	230	63	0.8	27.5	95.3
	2	"	"	5000	2.2	154	33	0.7	28.4	95.8
	3	"	"	8000	3.0	82	25	0.6	27.9	96.1
	4	"	"	10000	3.6	71	17	0.6	29.2	96.0
	5	"	"	12000	4.0	63	9	0.7	30.2	96.7

[Table 2]

		Polymer	Spinning Speed m/min.	Tenacity g/d	Elongation %	Boiling Water Shrinkage %	Periodic Irregularities Lengthwise Direction (cv%)
Comp. Ex.	1	PPT	4000	3.2	92	27	0.5
	2	"	6000	3.7	60	17	0.5
	3	"	8000	3.9	40	9	0.6
	4	"	10000	4.0	25	8	0.5
	5	"	12000	4.2	15	5	0.5

[0041]

[Advantageous Effect of the Invention]

The use of the manufacturing process of this invention for sheath-core conjugated fibers can substantially increase per unit hour throughput while suppressing any drop in fiber physical properties such as in Young's modulus, elongation recovery, and the like.

[Brief Explanation of the Drawings]

[Figure 1]

A graph showing stress-strain curves for fibers obtained by this invention and comparative example.

[Figure 2]

A graph showing stress-strain curves for fibers obtained by this invention and comparative examples.

[Figure 3]

A flow chart illustrating an example of the melt spinning process.

[Explanation of the Symbols]

- 1: Spinneret
- 2: Chimney
- 3: Oiling Guide
- 4: Entanglement Imparting Device
- 5: First Take-Up Roller
- 6: Second Take-Up Roller
- 7: Tensiometer
- 8: Winder

Figure 1

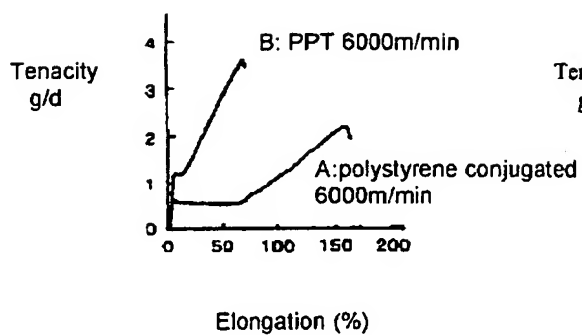


Figure 2

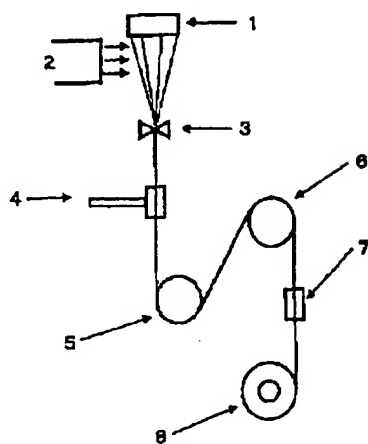
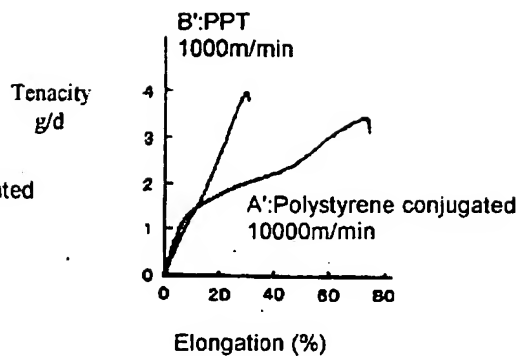


Figure 3

Trans: Language Services
Chemical Japanese Services
April 11, 2001